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ANALYSIS OF EXPLOSIVES IN SEA WATER AND  
IN OCEAN FLOOR SEDIMENT AND FAUNA

John C. Hoffsommer, et al

Naval Ordnance Laboratory  
White Oak, Maryland

September 1972

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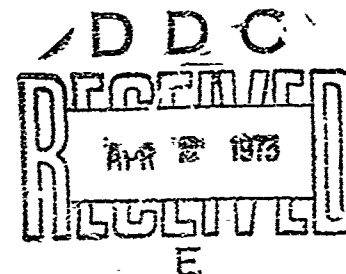
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John C. Hoffsommer  
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11 SEPTEMBER 1972



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NAVAL ORDNANCE LABORATORY, WHITE OAK, SILVER SPRING, MARYLAND

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Prepared by:

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ANALYSIS OF EXPLOSIVES IN SEA WATER AND IN OCEAN FLOOR SEDIMENT AND FAUNA

Ultramicro methods of analysis are described for the determination of explosive contaminants in oceanographic samples. The work reported is part of a broad environmental survey sponsored by the Oceanographer of the Navy and was funded by the Naval Oceanographic Office Work Request WR 2-0076.

ROBERT WILLIAMSON II  
Captain, USN  
Commander

ALBERT LIGHTBODY  
By direction

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## INTRODUCTION

The Oceanographer of the Navy has supported a comprehensive environmental survey of two ocean sites, in the Atlantic and Pacific, where surplus and obsolete munitions had been dumped in deep water (1). The survey goal was to determine whether the munitions had, in any measurable way, altered the environment. Our part of the task was to search for explosives contamination in the sea water and in the ocean floor sediment and fauna. In a previous closely related study, a method was developed for the quantitative analysis of explosives in sea water; and results were reported on sea water samples taken at two munitions dumping areas (2).

WEST COAST SURVEY

Sea water, sediment and ocean floor fauna samples taken in September, 1971, during the West Coast Survey of Deep Water Dump Sites XVI through XX were received at the Naval Ordnance Laboratory late in September. Water samples were stored in a refrigerator while sediment and fauna samples were stored in the freezer compartment. The refrigerator had never been used for storage of explosives, prior to its use for the oceanographic samples.

Description of Samples

## (a) Sea Water

<u>Sample Bottle</u>	<u>Station</u>	<u>Distance above Bottom, Meters</u>	<u>Location</u>
5	1	20	48° 16.3' N 127° 0.29' W
6	1	0	48° 16.3' N 127° 0.29' W
11	2	20	48° 22.8' N 126° 55.2' W
12	2	2	48° 22.8' N 126° 55.2' W

Water samples taken at stations 3, 4 and 5 did not survive shipment to our laboratory as they were packed in dry ice. The bottles were very badly cracked, to the extent the samples could not be used.

## (b) Sediment

<u>Station</u>	<u>Sample Depth, Meters</u>	<u>Location</u>
1	2621	48° 16.7' N 127° 05.8' W
2	2594	48° 22.2' N 126° 55.2' W
3	2588	48° 08.0' N 127° 04.7' W
4	2553	47° 50.5' N 127° 02.5' W
5	2043	48° 37.6' N 127° 00.5' W

## (c) Fauna

<u>Station</u>	<u>Trawl</u>	<u>Type</u>	<u>Location</u>
1	1	Rat Tail Fish	48° 17.9' N 127° 05.5' W
1	2	Sea Cucumber	48° 18.35' N 127° 00.8' W
2	3	Sea Cucumber	48° 21.5' N 126° 56.4' W
3	7	Sea Cucumber	48° 07.7' N 127° 04.8' W
5	10	Rat Tail Fish	48° 38.7' N 126° 57.5' W

We received no sample from station 4.

EAST COAST SURVEY

Sea water, sediment and ocean floor fauna samples taken in December, 1971, during the East Coast Survey of Deep Water Dump Site IX were received at the Naval Ordnance Laboratory late in December.

Description of Samples

## (a) Sea Water

<u>Sample No.</u>	<u>Station</u>	<u>Sample Depth, Meters</u>	<u>Location</u>
1	2 Lisa	958	31° 44.2' N 76° 54.4' W
2	2 Lisa	2086	31° 44.2' N 76° 54.4' W

## Sea Water (Cont.)

<u>Sample No.</u>	<u>Station</u>	<u>Sample Depth, Meters</u>	<u>Location</u>
3	2 Lisa	2150	31° 44.2' N 76° 54.5' W
4	2 Lisa	2167	31° 44.2' N 76° 54.4' W
5	2 Lisa	2215	31° 44.2' N 76° 54.4' W
6	2 Lisa	2242	31° 44.2' N 76° 54.4' W

## (b) Sediment

<u>Station</u>	<u>Depth, Meters</u>	<u>Location</u>
1	2255	31° 39.44' N 76° 55.74' W
2	2255	31° 43.95' N 76° 54.00' W

## (c) Fauna

<u>Type</u>	<u>Trawl</u>	<u>Depth, Meters</u>	<u>Location</u>
1 <u>Phormosoma</u> sp.	1	2500	31° 46.1' N 76° 52.0' W
6 <u>Bathypectinura</u> sp.;	1	2500	31° 46.1' N 76° 52.0' W

1 fish

## ANALYTICAL PROCEDURES

## A. Organic: TNT, RDX, Teteryl

## (a) Sea Water

The detailed procedure for the ultramicro analyses of TNT, RDX, and Teteryl in sea water samples is described in reference (2). However, briefly outlined: a 100 ml sample of sea water is extracted with 30 to 40 ml benzene; the benzene is evaporated to a small volume and injected into a research gas chromatograph equipped with a high temperature nickel 63 electron capture detector. Chromatographic traces of the sea water extracts are compared to the chromatographic traces of standard solutions of TNT, RDX, and Teteryl. Retention times and areas of peaks are measured by means of an automatic digital integrator to an accuracy

of  $\pm 1$  second for retention times and an integration area count of approximately 9 counts/mm<sup>2</sup>. Detection levels for TNT, RDX, and Tetryl have been determined to be 2, 5, and 20 parts per trillion, respectively, under normal routine working conditions.

(b) Sediment

A modification of the procedure given in (a) was used for the analyses of TNT, RDX, and Tetryl in sediment samples. Seventy-five to 100 grams of the sediment sample were stirred or triturated with 50 ml benzene depending on the sample consistency. The benzene extract was decanted into a 100 ml, r.b. flask for vacuum evaporation. Benzene extracts were centrifuged prior to evaporation only in those cases where the solutions were turbid.

After evaporation of the benzene extract under reduced pressure (17-20mm/20°C), the flask was rinsed with 1.0 ml of pesticide quality benzene and transferred to a 5.0 ml test tube. The benzene was again completely removed under reduced pressure. A total of 0.050 ml of benzene was added to the residue and after swirling and mixing the contents of the test tube, 0.025 ml of this solution were spotted along a narrow band in 5 separated spots onto a ChromAr 500 TLC sheet (glass fiber thin-layer chromatographic (TLC) paper consisting of 70 percent Silicar TLC 7F containing a short wave, 254 nm, UV phosphor on 30 percent glass fiber). Simultaneously, a standard mixture of TNT, RDX, and Tetryl in benzene was spotted to the right of this band, as a guide.

The fluorescent ChromAr sheet was developed in an ascending manner with hexane/acetone: 45/5 as eluent. After air-drying the ChromAr sheet in a hood for 5 minutes, zones for the standard TNT, RDX, and Tetryl were located as dark spots under 254 nm UV light. Corresponding areas to the left of these standards were cut out of the ChromAr sheet by means of a cork-borer, and transferred to a 5.0 ml beaker. These ChromAr discs were extracted three to four times with a

total of 1.0 to 1.5 ml of benzene by swirling and decantation. The benzene extracts were combined into a 2.0 ml sample tube with a tapered bottom and the benzene completely removed under reduced pressure (17-20mm/20°C). A total of 50  $\mu$ l of benzene was added to the tapered tube together with 5  $\mu$ l of o-dinitrobenzene ( $4.5 \times 10^{-10}$  g/ $\mu$ l) as internal standard. After thoroughly mixing, a 5 to 6  $\mu$ l injection of this solution was made into the gas chromatograph. At this point, the procedure follows that reported for the analysis of sea water.

(c) Fauna

Rat tail fish and sea cucumbers were analyzed for TNT, RDX, and Teteryl content with some modification of the procedure of that given in (2). Seventeen to 43.7 grams of the fauna sample was homogenized with 50 to 75 ml benzene in a Waring Blender for 5 minutes. This mixture was then centrifuged for 5 minutes and the supernatant benzene layer filtered through a Versapor membrane filter with a pore size of 1.2 microns (Gilman Instrument Company, Cat. No. 6429). The clear, slightly yellow-orange benzene filtrate was transferred to a clean, r.b. 100 ml flask and analyzed as in procedure (b). To make certain that the zones for TNT, RDX, and Teteryl would be completely separated from the organic dyes and other matter of the samples soluble in benzene, the ChromAr TLC sheets were developed a total of three times with a drying period of 10 minutes between each elution. Failure to completely separate these zones from organic interferences will cause high backgrounds in the vapor phase chromatographic traces.

By intentional injection of  $4.1 \times 10^{-7}$  g TNT,  $11 \times 10^{-7}$  g RDX, and  $17 \times 10^{-7}$  g Teteryl into a 51.4 gram sea cucumber, followed by subsequent work-up and analysis, limits of detection for TNT, RDX, and Teteryl are estimated to be 47, 123, and 740 parts per trillion, ( $10^{12}$ ) respectively.

## B. Inorganic: Ammonium Perchlorate

## (a) Sea Water

An analytical procedure has been established for the determination of ammonium perchlorate in sea water at a concentration down to one part per million. It is based on the use of an ion specific electrode, (Orion Research Corporation) which develops a potential across a thin porous inert membrane.

The potential measured is a function of perchlorate concentration. A reference curve is prepared using a standard (Copenhagen) sea water to which is added known amounts of perchlorate. Differences in sea water samples may contribute to a small uncertainty in the measurements, particularly at low concentration. For clear sea water, the method gives satisfactory results in the 1 ppm range, using a Beckman Research pH Meter.

Ammonium perchlorate may also be determined by a reaction with tetraphenylarsonium chloride which forms a very insoluble salt, tetraphenylarsonium perchlorate (3). The reaction produces a very distinct turbidity with 1 ppm ammonium perchlorate in sea water. With the aid of a Coleman Nephro-Colorimeter, one may obtain analyses approaching 0.1 ppm ammonium perchlorate. However, if the solution is too dark, this instrument cannot be used. In that case, the ammonium perchlorate can be determined visually by passing a narrow beam of light through a glass container with the finely divided tetraphenylarsonium perchlorate. About 0.1 ppm may be estimated reasonably well.

## (b) Sediment

A sediment sample of 25 to 35 grams was stirred with distilled water for several hours, after which the sediment was removed using a centrifuge. Ammonium perchlorate was measured by the turbidity of tetraphenylarsonium perchlorate.

## (c) Fauna

Water was used to extract ammonium perchlorate from the fauna samples of about 25 grams. Small pieces were stirred under about 100 ml water for at least eight hours. Small particles of fauna could not be removed from the water either by filtration or by separation using a centrifuge. However, these particles were coagulated with hydrochloric acid. To the clear filtered solution, tetraphenylarsonium chloride was added for a perchlorate determination. The ion specific electrode cannot be used with the fauna extract as a spurious reading is obtained.

## DISCUSSION

In none of the samples did we find explosive materials. The gas chromatograph described is a particularly sensitive instrument. If explosive contaminants are present, they must be at concentration levels below those previously stated. In the case of water samples, only the two lowest level samples were analyzed. Other levels were sampled to obtain a vertical distribution of the explosive contaminant, and were to be analyzed only if explosives were detected in the bottom area. It is quite fortunate that water samples from station 1 off the west coast were received as this station represents the center of the dumping area. If explosive contaminants are not present in the center of the dumping area, the probability is near zero that any would be found from 2 to 15 miles away from the center.

In any project dealing with trace detection and determination of chemical species, extreme care must be used in the selection of sample containers and in the actual handling of the samples. Instructions were provided for shipboard personnel taking the samples. That these instructions were followed was substantiated by the relatively low background "noise" in the gas chromatograph traces.

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Samples in the Pacific area were taken by Naval Oceanographic Office personnel; samples in the Atlantic area were taken by Naval Research Laboratory personnel. Valuable assistance was provided by LTCDR Ronald C. Tipper, on the staff of the Oceanographer of the Navy.



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2. John C. Hoffsommer and Jerome M. Rosen, "Analysis of Explosives in Sea Water," Bulletin of Environmental Contamination and Toxicology, 7, 177 (1972).
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APPENDIX A

SAMPLE HANDLING INSTRUCTIONS

Use new Pyrex bottles, 250 to 500 ml size, with a Standard Taper Stopper. The bottles should be washed with soap and water and then given at least five rinses with good quality water. Do not touch the ground glass surface of the stopper, or allow the surface to touch any contaminant. When necessary, the stoppers may be placed on aluminum foil, which provides a good clean surface. Rinse the bottles at least twice with 50 to 60 ml of the sea water sample to be returned. Finally, fill the bottle and hold the stopper in place with a sturdy tape. Electrical insulating tape works very well. Store the samples in a cool dark place prior to return for analysis. Do not freeze. Wide mouth bottles should be used for the fauna samples. The bottles should be new and the same meticulous care used in cleaning and handling these as the other sample bottles.